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LUMINOUS AND FLUORESCENT PAINTS

This letter circular has been prepared as a result of the numerous requests received by the Bureau for general information regarding luminous and fluorescent paints. These two types of material, which are designed to emit light under certain conditions are described respectively under the headings used in the title, although in certain instances there is no sharp line of demarcation between the two.

It is not the intent of this letter circular to tell how to manufacture luminous and fluorescent pigments and paints. The manufacture of these products requires a high degree of technical skill in selecting and purifying the raw materials and in the proper methods of processing the mixture. With regard to the purity required, it is known that the presence of exceedingly small amounts of certain elements is sometimes fatal to luminescence.

The National Bureau of Standards has made no systematic investigation of luminous and fluorescent paints, other than the one referred to later under (b) Radioactive Paint, but has compiled the following information which may be found useful.

1. Luminous Paint

Luminous paint may be classified further into two groups, one designated as phosphorescent and the other as radioactive. Phosphorescent powder or paint, after exposure to ultraviolet or visible radiant energy, may continue to glow for a few minutes to several hours in the dark. The material may be reactivated by exposing it again to the exciting stimulus. Contrasted with this, the radioactive pigment or paint does not require any such exposure but is continuously activated by the radioactive material it contains.

(a) Phosphorescent Type.- The phosphorescent type of luminous paint may contain for a base, or phosphor, specially prepared impure sulfides of calcium, strontium, barium or zinc, or certain mixtures of these materials. The property which they exhibit - luminescence after irradiation - is known as phosphorescence. The more or less prevalent idea that phosphorescent paints contain phosphorus is erroneous. Luminous paint can not be made from this substance, which is very dangerous to work with.

The pure sulfides do not phosphoresce, so that apparently this property is due to the presence of minute quantities of foreign substances. Traces of certain elements, such as copper, bismuth, lead, cadmium, manganese, samarium, cobalt, nickel, etc., designated as "activators", serve this purpose and also impart a characteristic color to the glow of the basic material. Luminous strontium sulfide generally has a strong greenish blue phosphorescence, luminous calcium sulfide a violet color, luminous barium

sulfide a yellow-orange color, and luminous zinc sulfide a yellowish green color. Phosphorescent pigments are relatively coarse in particle size, and paint films made from them are somewhat rough. Any attempt to grind the pigments to a fine state of subdivision is apt to result in a serious decrease in phosphorescence.

The nature of the pigment also determines the intensity and duration of the afterglow. For example, certain pigments which have a relatively intense initial brightness during irradiation have a shorter time of useful afterglow (usually two hours or less). Zinc sulfide and zinc-cadmium sulfide are illustrative of this property. Contrasted with this, the alkaline earth sulfides, for example, luminous-calcium sulfide and luminous-strontium sulfide, have a lower initial phosphorescent brightness, but a longer useful afterglow (usually from two to twelve hours).

In making a phosphorescent paint, it appears to be common experience that the ordinary, or oleoresinous, varnishes, and most drying oils are not suitable liquids. Likewise the usual metallic driers will often give trouble. Strontium sulfide will not tolerate any heavy metal drier, while zinc sulfide is adversely affected by cobalt. In the latter case the use of manganese or lead, in that order, is suggested. They may also be used in combination. The liquid or vehicle must be practically neutral, and in some cases must be selected with the pigment in mind with which it is to be used. Cellulosic lacquers, spirit varnishes (alcohol-shellac varnish), dewaxed dámar varnish and vehicles prepared from plasticized chlorinated rubber, cyclohexanone resin, vinyl resin and polystyrol resin, suitably plasticized, may be used. The last named resin plasticized with dibutyl phthalate and dissolved in xylol is said to make one of the best vehicles for phosphorescent paint for outdoor use.

Application and Uses of Phosphorescent Paints.- The usual practice is first to apply to the clean wood, metal or fabric surface a special white primer or undercoater paint composed of titanium oxide (not the nonchalking type), barytes and similar nonreactive pigments in a special vehicle, for example, the polystyrol resin vehicle mentioned previously. After this is dry the phosphorescent paint is applied. If thinning is necessary, a special thinner provided by the manufacturer should be used. Care should be taken that an absolutely clean and dry brush is used with each paint. After this paint is dry, a transparent, protective, special varnish (plasticized polystyrol resin dissolved in xylol for example) supplied by the same manufacturer, is sometimes necessary to protect the luminous paint from moisture and the weather. This point is covered in the manufacturer's directions.

The surface ot which the phosphorescent paint is applied may affect the luminosity of the paint. Therefore, the surface must be clean, dry and neutral or nonreactive to the paint. This is one reason for using a special undercoater supplied by the manufacturer of the phosphorescent paint. Because the surface as well as the application of the paint can be controlled better at the factory, objects such as oilcloth, paper, cardboard, wallboard, decalcomanias, etc., all coated with the phosphorescent paint, are available. Likewise, markers made of transparent plastics (for example, vinyl resin or methyl methacrylate resin plastics) impregnated with the phosphorescent pigments are available.

In order to forestall disappointments which might arise from what appear to be rather general misconceptions regarding the possible uses and properties of the phosphorescent type of luminous paint, the following statements are offered as a guide. When considering such a suggestion as painting roads and curbs with it in order to increase visibility at night (a suggestion frequently heard), it is well to remember, first of all, that the paint is relatively expensive. One well-known brand, at the present writing sells for $24 a gallon. Again, it should be remembered that the afterglow is of relatively low brightness and is best appreciated in complete darkness, where its effect may be quite striking. The presence of light from any other source serves to decrease this effect very markedly. The obvious conclusion is, therefore, that the use of this material ordinarily should be confined to objects located indoors, or in nearly complete darkness, such as light switches, stair treads, shelter entrances, guide railings or lines, doorknobs, etc. These uses are in addition to the many others for which the previously-mentioned prefabricated type of luminous marker may be used, such as arm bands, insignia and various other identifying marks.

Note: Where certain conditions exist which make phosphorescent materials unsatisfactory, the use of fluorescent materials is suggested, and the reader is referred to that section.

(b) Radioactive Type.- The luminous paints that are used today for painting the numbers or letters on watch and clock dials, compasses, etc., contain a minute amount of radioactive substance such as radium or mesothorium on a responsive base, usually zinc sulfide. The amount of radium required is very small and may be of the order of one part of radium to 20,000 parts of the base. Its purpose is to excite the base continuously so that no prior exposure to radiant energy is necessary. The vehicle generally consists of a special cellulosic lacquer or a synthetic resin varnish, such as plasticized vinyl resin, or polystyrol resin dissolved in a suitable solvent. A paint of this type is naturally more expensive than one of the phosphorescent type.

In addition to its use in a paint, the radioactive pigment has some times been placed between two disks of transparent synthetic resin plastic, in the form of "buttons" about one inch in diameter, which are used as guide markers on a road during blackouts.

It is emphasized here that radio active pigments have caused serious injury to factory workers and extreme caution must be used in preparing them. The Bureau of Labor Statistics of the Department of Labor has made two surveys to investigate the startling developments of radium poisoning among workers applying luminous paints to clock and watch dials. Summaries of these are given in the Monthly Labor Review for May 1926 and June 1929.

Some recommendations have been made by State factory inspectors to individual establishments engaged in such work for extreme caution in methods and in handling the materials. Legislation in connection with the subject has been enacted in regard to workmen's compensation. The many cases appearing in New Jersey resulted in the addition of radium-mesothorium necrosis to the list of compensatable occupational diseases in that State in 1927, and in 1930 the State of New York included radium poisoning as a compensatable occupational disease.

(c) References.- The following references contain information on luminous pigments and paints:

Government Publications

The National Bureau of Standards has published a booklet designated as Handbook #27, "Safe Handling of Radioactive Luminous Compound", dated May 2, 1941. This booklet can be purchased from the Superintendent of Documents*, Government Printing Office,

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* When ordering publications from the Superintendent of Documents the application should be accompanied by money order, coupon or cash (not stamps). The coupons, which are good until used, can be bought from him at $1.00 for 20.

Washington, D. C., for 10 cents. Likewise this Bureau has issued Letter Circular 550, dated April 1, 1939 on "Fluorescence and Phosphorescence", a copy of which may be obtained free by writing to the Bureau.

In addition there are three Government specifications for radioactive luminous material. One is Navy Department Specification 52R9a, dated January 2, 1940, a copy of which may be obtained upon application to the Bureau of Supplies and Accounts, Navy Department, Washington, D. C. Another is U.S. Army Specification 3-99D, a copy of which may be obtained upon application to the Army Air Corps, Material Division, Wright Field, Dayton, Ohio. The third is Federal Specification TT-R-58, a copy of which may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C., for 5 cents.

The Ordnance Department, War Department, has issued a specification for luminous paint of the phosphorescent type (not radioactive) identified as "Rock Island Arsenal Tentative Specification RIXS-122 Paint, Luminous, Non-Radioactive", dated January 24, 1941. The British have issued British Standard Specification BS/ARP 18, "Fluorescent and Phosphorescent Paint", dated July 1940. A copy may be purchased for 50 cents from the Canadian Engineering Standards Association, Room 3010, National Research Building, Ottawa, Canada. The Engineer Board, War Department, Fort Belvoir, Virginia, is developing a specification for luminous paint of the phosphorescent type, and it is expected that eventually a Federal Specification will be prepared. The Material Division, Army Air Corps, Wright Field, Dayton, Ohio, has prepared Specification No. 14102, "Lacquer Fluorescent, Instrument Marking", dated June 26, 1940, and Specification No. 17012, "Markers, Fluorescent, Instrument Identification and Range," dated July 19, 1940.

Paints containing radioactive substances were studied by the National Bureau of Standards during 1917-1920, primarily for military purposes. With the exception of a brief report issued by the National Advisory Committee for Aeronautics (Fourth Annual Report, 1919), the results have not been published.

Dorsey, N.E., Self-luminous materials, Report No. 33 in Fourth Annual Report, National Advisory Committee for Aeronautics, 1920. Out of Print.

Curtiss, L. F., Brightness meter for self-luminous dials, J. Research, National Bureau of Standards 15, 1 (1935) RP 804. Price 5 cents.

Publications Other than Government

Raaland, E. R., Luminous Paints and Colors, American Paint Journal (St. Louis, Mo.), vol. 24, no. 34, p. 18, June 9, 1930.

Parson, A. T., Radium, with special reference to luminous paint, Journal Oil and Colour Chemists Assn. (London, England), vol. XII, p. 2, 1929.

Gardner, H. A., Van Heuckeroth, A. W., and Faust, J. B. Some notes on luminous paints, Cir. No. 272, Paint Manufacturers' Assoc. of the United States (Washington, D. C), May 1926.

Barry, J. Hedley, Luminous paint, The Decorator (London, England), September 1928.

Bearn, J. C., Luminous paints, Paint and Varnish Production Manager (New York, N.Y.), vol. 5, nos. 4, 5 and 6.

Bryson, H. Courtney, Luminescent pigments and paints, The Paint Industry Magazine, 1524 Chestnut Street, Philadelphia, Pa., February, March and April 1940. Also in the Official Digest, 220 South 16th Street, Philadelphia, Pa., February and March 1940.

Petzold, O., Phosphorescent paints, Paint Manufacture (British), vol. 10, p. 7, January 1940.

Fain, J. Mitchell, Luminescent paints, News Ed., (Am. Chem. Soc.), vol. 19, no. 22, p. 1252, 1941.

Millson, Henry E., Black-Out Preparations in the United States, News Ed., (Am. Chem. Soc.), vol. 19, no. 22, p. 1266, 1941. (Also abstracted in the American Ink Maker, Jan. 1942, p.29.)

Sub-Committee No. 43 of the Technical Committee of the New York Paint and Varnish Production Club, Federation of Paint and Varnish Production Clubs, has issued a report entitled "Luminescent Coatings.". The chairman of this sub-committee is Dr. J. J. Mattiello, Hilo Varnish Corporation, 42 Stewart Avenue, Brooklyn, New York.

2. Fluorescent Paint

The essential distinction between fluorescent and phosphorescent materials is in regard to the length of time that light is emitted after removal of the exciting source. From the practical standpoint, fluorescent materials emit light only during irradiation, and it is upon this property, together with the fact that they may be irradiated by ultraviolet energy, popularly known as "black light", that their usefulness depends. (Actually, there may be an extremely short period of afterglow, even for fluorescent materials, but according to Demant and Petzold* this must not exceed one millionth of a second, to fall in this category). As

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* Fluorescence and the Black-Out, Paint Manufacture (British), vol. 10, p. 23, Feb. 1940.

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with phosphorescent pigments and paints, emission of light of various colors (red, green, blue, yellow, etc.) is possible with a given exciting source, depending on the nature of the material. The intensity of the fluorescence is proportional to the intensity of irradiation. Some of the more common pigments used in fluorescent paints are zinc sulfide and zinc-cadmium sulfides. Zinc silicate, alkaline earth sulfides, tungstates, uranyl salts, boric acid, organic dyes (rhodamine, eosine, thioflavine, auramine), etc., possess fluorescent properties. To some of these are added small amounts of certain heavy metals such as copper, manganese, lead, bismuth, silver, etc., or organic compounds, depending on the nature of the base, which serve as activating agents. A typical fluorescent pigment is zinc sulfide activated with a small

amount of copper. The zinc sulfide first is prepared in very pure form. To the dry zinc sulfide is added 5 to 10 percent of a flux (for example, sodium chloride) and the activating copper (in the form of an aqueous solution of a copper salt). The mixture is then heated to about 1000° C. Such combinations are known as phosphors or luminophores. Some of the more generally used phosphors and the colors of light they emit when irradiated with ultraviolet energy are: strontium sulfide-bismuth (green), barium sulfide-bismuth (yellow), calcium sulfide-bismuth (violet), and zinc sulfide-copper (green). A blend of 75 percent of zinc sulfide and 25 percent of cadmium sulfide activated with a small amount of copper gives a red fluorescen

Application and Uses of Fluorescent Paint

The same general considerations which govern the application of phosphorescent paints apply as well to fluorescent paints and the reader is referred to that section.

Fluorescent materials have come into use where positive illumination of detail in darkness is required, as in the case of instrument dials in airplanes, printed maps, train schedules, printed signs, etc. The printed material may be produced commercially in large quantities. All of these may be read in the dark by means of small commercially available "black lamps" such as 2.5 watt argon lamps and other types of black light sources. Fluorescent plastics, cloth, paper, carpets, etc., are also available, and are caused to glow in the same manner.

The following articles have appeared recently (1940) on the subject of fluorescent pigments and paints:

Demant, V. and Petzold, O., Fluorescence and the Black-Out, Paint Manufacture (British), vol. 10, p. 28, February 1940.

Fluorescence Efficiency, ibid., p. 60, March 1940.

Fluorescent Pigments, ibid., p. 86, April 1940.

Fluorescence and the Blackout, ibid., p. 134, June 1940.

Formulation of Fluorescent Paint, ibid., p. 174, August 1940.

(See also the applicable references under Luminous Paints.)

3. Sources of Supply

Phosphorescent and fluorescent pigments and paints can probably be furnished by:

Pfaltz & Bauer, Inc., 300 Pearl St., New York City.

American Luminous Products Co., Huntington Park, Calif.

Maas and Waldstein Co., 438 Riverside Ave., Newark, N. J.

Sylvania Electric Products, Inc., Salem, Massachusetts.

Hammer Labs., Inc., Central Savings Bank Bldg., Denver, Colo.

Merck & Co., Inc., Lincoln Ave., Rahway, N. J.

Prescott Paint Co., 445 West 41st St., New York City.

Fluorescent Pigments Corp., 445 West 41st St., New York City.

Luciphor, Inc., 114 East 28th St., New York City.

Fairmount Chemical Co., 126 Liberty St., New York City.

New Jersey Zinc Co., 160 Front Street, New York City.

Flame-Glo Company, Inc., 135th Street and Willow Ave., New York City.

Phantom-Glo Co., Los Angeles, Calif.

General Luminescent Company, Chicago, Ill.

Patterson Screen Co., Towanda, Pennsylvania.

Lunex Corporation, Cleveland, Ohio.

Continental Lithographic Co., Cleveland, Ohio.

Stroblite Corp., 52 W. 52nd Street, New York City.

Harshaw Chemical Co., Cleveland, Ohio.

Millmaster Chemical Co., 551 Fifth Ave., New York City.

Cruver Mfg. Co., 2465 W. Jackson Blvd., Chicago, Ill.

Defense Blackout and Camouflage Co., Inc., 2265 Bedford Ave., Brooklyn, N. Y.

Grobet File Corp. of America, 3 Park Place, New York City.

The House of Simes, 13 So., 13th Street, Philadelphia, Pa.

Radioactive pigments, and vehicles for them, can probably be furnished by:

U. S. Radium Corp., 535 Pearl St., New York City.
Radium Chemical Co., 570 Lexington Avenue, New York City.
American Luminous Products Co., Huntington Park, Calif.
Radium Luminous Corp., 10 East 40th St., New York City.

Canadian Radium & Uranium Corporation, 630 Fifth Ave., New York City.

Hammer Labs., Inc., Central Savings Bank Building, Denver, Colorado.

Luma Incorporated, 305 E. 46th Street, New York, N. Y.

Rhode Island Laboratories, Inc., 100 Pulaski Street, West Warwick, Rhode Island.

Warner-Martin Corporation, 560 Harrison Avenue, Boston, Mass.